

pronounced the gradient is less, and in extreme cases is practically non-existent.

2. *Susceptibility measured at Right Angles to the Direction of the Compressive Force.*—Rock specimens whose normal susceptibility varies from 1.6 to 0.0016 have been tested at pressures varying from 250 to 390 kgrm. per square centimetre. In all cases in which a variation has occurred it has been to slightly increase susceptibility with increase in pressure.

The Properties and Molecular Structure of Thin Films.

Part II.—*Condensed Films.*

By N. K. ADAM, M.A., Sorby Research Fellow at the University of Sheffield;
Fellow of Trinity College, Cambridge.

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1. *General Structure of the Films.*

In this and a following paper, an account will be given of work done in continuation of the experiments on thin films of palmitic acid, described in Part I of this investigation (1), and, in particular, of the results obtained by extending the range of substances composing the films, and the range of temperature over which the experiments were made. As was there pointed out, the study of these films is a peculiarly attractive one, owing to the extremely simple manner in which the molecules are arranged; the films

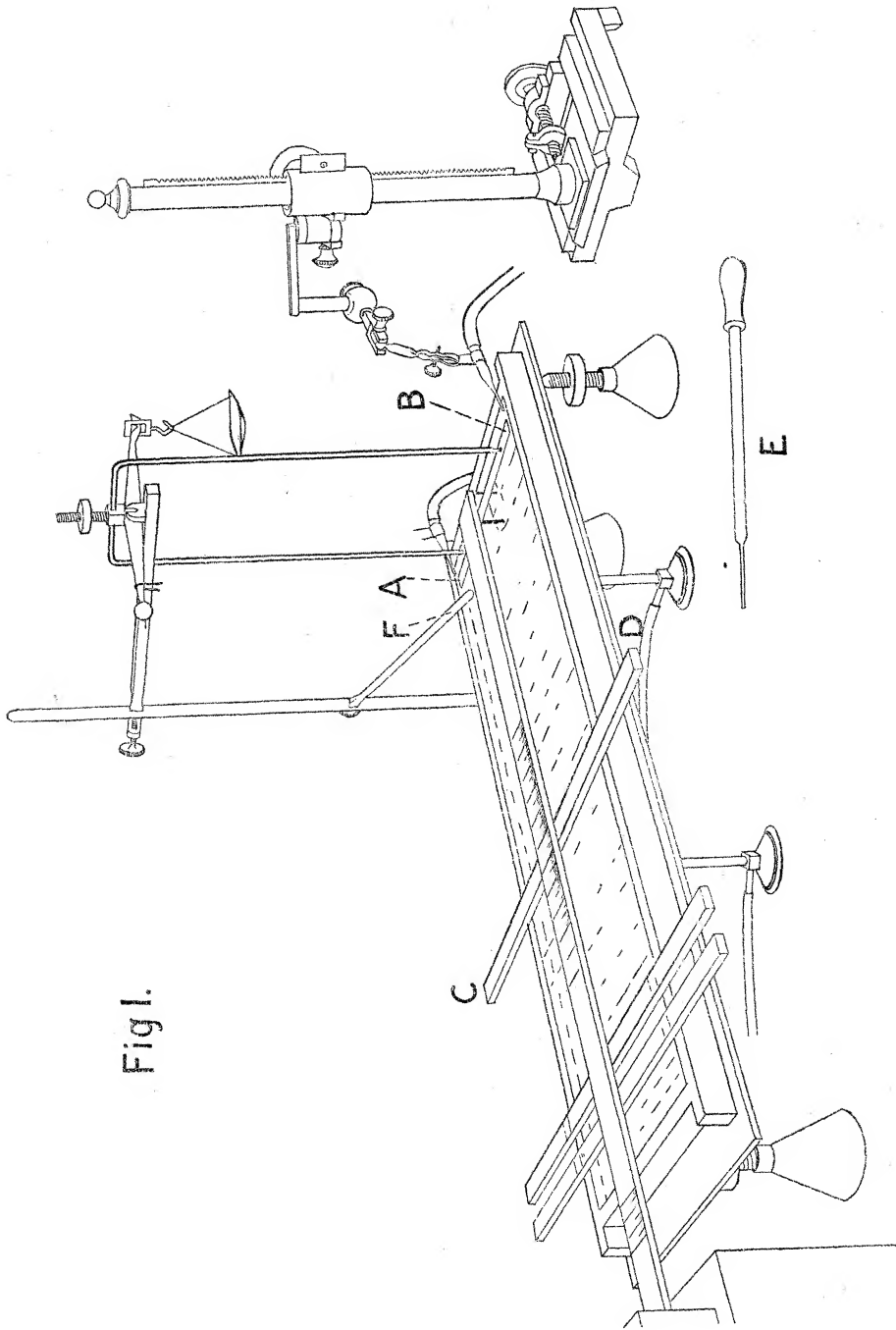
being of one molecule in thickness and the molecules in them being arranged not indiscriminately, but perpendicular to the surface and parallel to each other, as a rule. The experimental method (due in principle to Langmuir) has also a great advantage over those more commonly employed in capillary studies, that the forces tangential to the surface are measured directly. Exceptionally direct information is therefore obtainable as to some of the forces between the molecules composing the films, and by a study of the influence of chemical constitution on the properties of the films, much light should be shed upon the important problem of the relation between chemical and capillary forces.

It will not be necessary to occupy space in proving that, for any of the substances here studied, the films are one molecule in thickness. Reasons for taking this view have been given by other workers, as well as on p. 344 of my preceding paper, and it is sufficient to say that the experiments described here afford evidence of the same character, which is equally conclusive for each one of the substances investigated.

The general arrangement of the experiment has been as before, and is shown in the drawing (fig. 1). Some points of detail to which attention is necessary in conducting experiments are noted in Section 15. It is desirable, however, before proceeding to the discussion of the results obtained, to make clear what is the interpretation which will be adopted of the forces acting on the balance float which bounds one end of the film.

Previous to putting on the film, the surface is cleaned by means of the barrier CD, sweeping away all contamination to the left. A clean surface possesses the property that CD may be moved right up to the float AB without any repulsion occurring before contact. In practice, this degree of cleanliness has been very nearly approached. A known quantity of the substance under examination is immediately put on, dissolved in a volatile solvent, which first serves to spread it in a uniform film over the whole of the available surface, and then evaporates in a few seconds. It is found that the film remaining will transmit a force of repulsion from the glass barrier to the float, and that the film possesses a definite area at a given force. The curves called "compression curves" exhibit the force on the float AB in dynes per centimetre as ordinates, and the areas per molecule in the film as abscissæ. The areas will be expressed in terms of the unit 10^{-16} sq. cm., which will be denoted by Å.U., following Sir W. H. Bragg (2).

This force will be regarded simply as a force of compression acting on the film; the film, *as a whole*, and any other floating objects, being considered as not subject to any tangential forces whatever by the water. The film of molecular thickness covering a portion of the surface will be regarded in much



the same way as any other body floating on the surface. Force transmitted from the barrier CD to the float AB is conveyed as a thrust in the floating film. A perfectly simple picture is obtained in this way of the part played by each molecule in the film, and the forces acting upon it. Each one is attracted strongly to the water, particularly by the polar group directed towards it; the hydrocarbon chains, which are arranged more or less perpendicular to the surface, exert a lateral attraction upon each other, and these two sets of forces appear to be the principal factors in determining the stability of the film. They are so powerful that the film will resist, without serious deformation in many cases, very considerable forces of compression laterally; it will be evident presently from the diagrams that forces of over 45 dynes per centimetre are occasionally withstood before buckling takes place, and this, calculating from the thickness of the films, is over 200 atmospheres. Finally, the observed force of repulsion on the float AB is the direct result of all the inter-molecular forces of repulsion acting between the individual film molecules, and therefore the area of the films under a given compression affords direct evidence as to the cross section of those parts of the molecules which are in contact. It will appear, later, that there is much evidence that many of the molecules studied, though their general shape is highly elongated, have not the same cross-section at all points of their length; and an attempt has been made to estimate the maximum cross-section of many of the polar groups, which appear as a rule to be somewhat wider than the hydrocarbon chains.

While in the preceding paper, over the limited range of temperature studied, it appeared correct to consider the films as composed of molecules in direct contact with one another over the whole area, and therefore the thermal movements among the molecules could be to a large extent neglected, just as can the vibrations of the atoms composing a crystal, in the discussion of their general arrangement in the second of these two papers it will become necessary to take account of these thermal movements. In every one of about twenty substances studied, when the temperature of experiment was sufficiently high, a definite change took place in the properties of the film, resulting in a considerable increase in the space occupied per molecule. This change was identical with that previously described by Labrouste (3), and the further study to be described in Part III has shown that its principal features were the same for all the molecules investigated, which had only one feature in common, namely, a hydrocarbon chain of 12 to 22 carbon atoms in length. This change appears almost certainly to be a separation of the molecules from one another in the surface, brought about by the thermal agitation becoming so violent that the lateral attractions of the molecules for each other (already

referred to as one of the main stabilising forces in the films) are overcome. The films in this state will be designated "expanded films"; their properties in many respects are those of a gas, or rather vapour, in two dimensions; and at temperatures close to that at which the expansion takes place, transitional phenomena are observed analogous to those attending the passage from the liquid to the vapour state; the isothermals (connecting, of course, compression and area) closely resembling the isothermals of a vapour near the critical point. It has been mentioned that the main features of the expansion are the same for all the films studied; it will appear later that there are important differences in detail which can, on the one hand, be certainly correlated with the length of the hydrocarbon chains, and therefore with the magnitude of the attractive forces between the individual film molecules; and, on the other, very probably, with the magnitude and nature of the forces exerted by the molecules of the underlying solution (or water) on the parts of the film molecules in most immediate contact with them, and thus probably with the forces which are operative between solute and solvent molecules in a solution. Those films in which the molecules appear to be in direct contact over the whole area will be designated "condensed films."

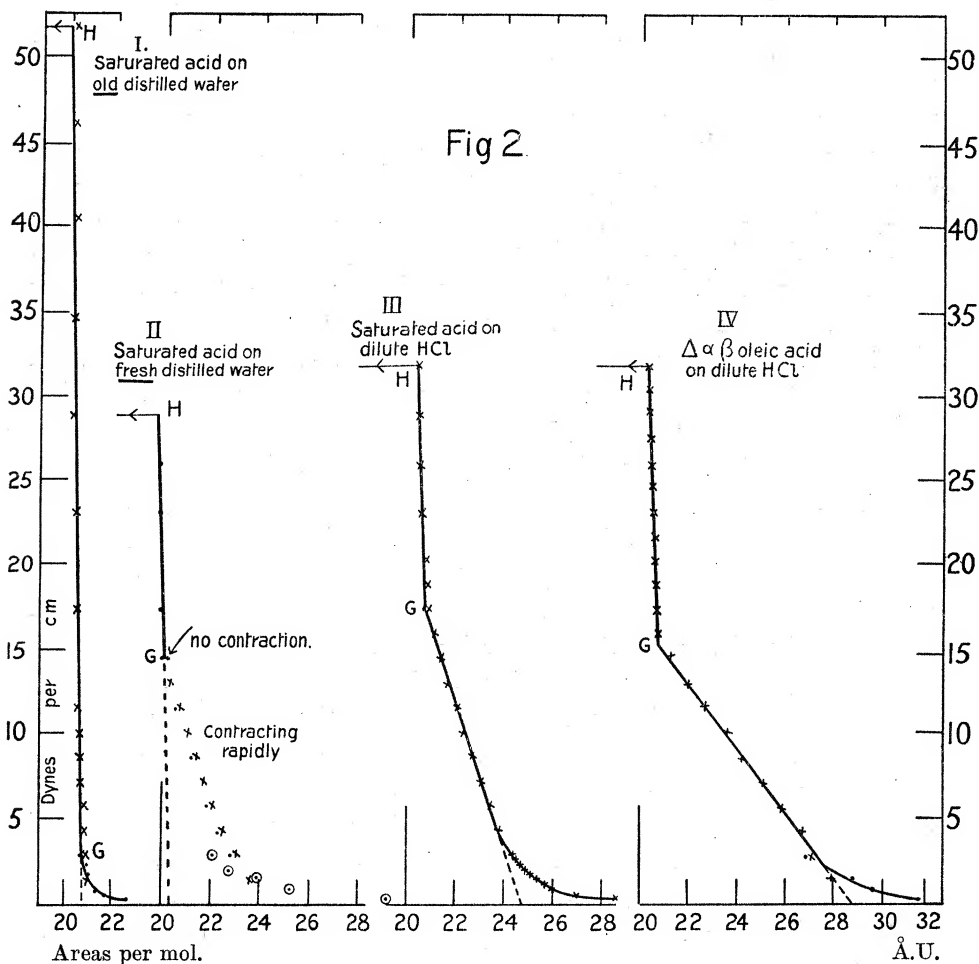
I am most deeply indebted for the supply of materials to several friends, and, in particular, to Dr. E. F. Armstrong, F.R.S., Prof. A. Lapworth, F.R.S., Miss M. Stephenson, and Mr. C. C. Wood. To the last named I owe permission to use the invaluable collection of long-chain compounds prepared by the late Dr. H. R. Le Sueur at St. Thomas' Hospital. This assistance has made it possible to extend the scope of the investigation far beyond what I could have done unaided, and has therefore made what results have been attained much more satisfactory. To my wife I am indebted for preparing diagrams in these and other papers; and for much other assistance to other friends. I am indebted to the Government Grant Committee for a grant covering most of the cost of this investigation.

In figs. 2 to 4 are given the compression curves of the substances which have been investigated most fully up to the present; all these curves are (as will be shown) to be regarded as those of condensed films.

2. *The Fatty Acids on Distilled Water.*

Fig. 2 is of substances which contain the free COOH group, and the curves I and III are identical with the curves given in my preceding paper, determined on palmitic acid only. They are reproduced here, as their form has now been determined at compressions lower than the lowest previously recorded, and also because many more experiments have shown that the slope previously given was not quite steep enough.

Curve I is what was obtained on distilled water *which had been in the trough several days*. It was found to be exactly the same for the following acids;



myristic, pentadecylic, palmitic, margaric, stearic, heneicosoic, and behenic (the saturated acids C_{14} to C_{22} with the exception of C_{19} and C_{20} which were not available), and for the isomer of oleic acid which has the double linkage between the α - and β -carbon atoms. The phenomena presented by the commoner unsaturated acids, which have the double bond in the middle of the chain, have not yet been sufficiently worked out, but it may be said that under certain circumstances some of them give a compression curve which closely resembles this one, and I am now doubtful whether the conclusion drawn by Langmuir and accepted by me (4), that these acids form films in which the double bond itself occupies a definite area on the water, providing

a second point of attachment for the molecule, will prove to be capable of explaining the phenomena.

Three other saturated acids were tried, lauric (C_{12}), tridecylic (C_{13}), and cerotic (C_{26}). The first two gave results approximating to the same curve as the other acids, but complicated by the steady shrinkage of the films through solution of the molecules in the water. The best specimen of cerotic acid which I could obtain gave a film which did not spread properly in benzene solution on the surface, and the film showed a constant tendency to contract, with the appearance of the aggregates characteristic of the collapse of a monomolecular film of the lower acids when the compression is high enough to buckle the film. It may be that the specimen was not pure enough, or perhaps the chains are so long that their lateral attraction for one another is sufficient to drag the molecules away from the water, into the aggregates, spontaneously. The area per molecule was, however, roughly the same as that of the other acids of the series.

It will be noticed on close inspection that the curve is not quite straight. The line drawn is straight, and the points lie somewhat to the right of it at the top and at the bottom, showing that the compressibility decreases slightly at higher compressions. It is always however very small, and comparable with the compressibility of liquid paraffin in bulk, as was previously shown. The figure given in the previous paper for the compressibility was too great; the apparatus is not of course suited for accurate measurements of such small compressibilities, and it must be remembered that any error such as undetected leakage past the barriers, or slight collapse of the monomolecular film locally will increase the observed compressibility, so that in estimating the order of magnitude preference should be given to low values. The earlier value was 1.7 per cent. decrease in area for 10 dynes per centimetre. This has since been found to be exceptionally high for a good experiment. Usually it is about 0.8 per cent., and in some instances, on chains of 18 carbon atoms and upwards in length, values as low as 0.4 per cent. have been found. The earlier value recorded was about five times the volume compressibility of $C_{15}H_{32}$ so that the later observations show the true compressibility in this portion of the curves to be nearly the same as that of this liquid in bulk.

3. *Cross Section of a Hydrocarbon Chain.*

Though the very nearly straight line GH in fig. 2, curve I, is nowhere duplicated in its full length, parts of it are very common in the upper portions of the compression curves of condensed films. It has been found in all those given here, except with stearic nitrile and the substituted ureas below a transition temperature which will be later noted. Once the state corre-

sponding to GH has been attained, it continues as the compression is increased until collapse at H takes place. Produced to meet the line of no compression, this curve cuts it at 21.0 Å.U. This figure is the mean of a large number of experiments on twenty different substances, all the observations being between 19 and 23, and the majority between 20 and 22 Å.U. I have included in some of the curves the points corresponding to typical duplicate experiments, in order to give an idea of the accuracy which is obtainable when working with the greatest care. There is usually rather more error in knowing the amount of material put on than in determining the relative areas under different compressions, as is shown by the fact that the points not on the curves in fig. 3, I and III, lie on curves parallel to those drawn in. Different experiments are indicated in the diagrams by different kinds of points.

The area of the intersection 21.0 Å.U. is probably correct within a few decimals, unless there is any constant error in the experiments. Two possible sources of such error should be discussed. In the previous paper a correction was applied for the residual contamination left after cleaning the surface before putting on the film, by determining approximately its amount before putting on the film and subtracting the area it occupied from the observed area of the film. Probably the amount subtracted was too great, perhaps much too great, since it has been found extremely difficult in later work to detect any difference between uncorrected curves determined on surfaces on which there was not more than 2–3 mm. of residual contamination at 1.4 dynes per centimetre, and where five times this quantity was present. If the correction were correct one would have expected a difference in area at about 5 dynes per centimetre of about 0.5 unit, and the determinations of the area of intersection might be on the average about 0.3 unit too great, taking a liberal estimate of the average amount of contamination which has remained on the surfaces in this series of experiments. But since the correction is probably a good deal too high, it is unlikely that residual contamination has made the determination of this average value as much as 0.2 Å.U. too great.

The influence of the air blasts at the ends of the float AB (fig. 1) might also have made the observed area slightly too great by blowing the film away from the barrier, so that what was really a bare patch was taken as covered by the film. The amount of error from this cause was probably very small indeed. It was impossible to see directly how far the film was blown back; but when a solid film such as tripalmitin was put on, and talc sprinkled on the surface, the area in which the solid structure was destroyed could be seen. It did not amount to more than a correction of about 0.2 Å.U. on an average size of film. The area completely cleared must have been much less. Possibly a rigid film is blown back less than a liquid one, but the error does

not seem to be large. The strength of the air blasts has been adjusted so as to be not much more than that necessary to prevent leakage.

The low compressibility in GH must indicate that the film molecules are not appreciably displaced relative to one another during compression. It has already been calculated, on certain assumptions,* that the cross-section of a CH_2 group perpendicular to the general direction of the chain is about $19.3 \text{ \AA.U.}$ Probably, then, for all the films in which this portion of the curves appears, the molecules have their hydrocarbon chains closely packed in the last stages of compression which precede collapse; and in many cases the chains are closely packed under quite small compressions. The figure $21.0 \text{ \AA.U.}$ is thus obtained as the cross-section of a hydrocarbon chain as packed in the films, any error being probably so small that the true value is not greater than 21.2 or less than $20.5 \text{ \AA.U.}$

4. *Fatty Acids on Dilute HCl.*

The strength of the solution is of little importance, and the following remarks apply to $\text{N}/10$ and $\text{N}/100$ HCl solutions equally. Fig. 2, III, is the curve obtained with all the fatty acids examined, except the saturated ones of 12, 13 and 26 carbon atoms, iso-oleic acid ($\Delta\alpha/\beta$ oleic acid), oleic, elaidic and erucic acids. Brassidic acid, although it has a double bond in the middle of the chain, does give this curve, and the curves of elaidic and erucic acids, at temperatures near 0° , are intermediate between this curve and those to be described in Part III as typical curves of expanded films, and indicate that, if experiments could be done a few degrees below 0° , these films would be condensed, and would show the same curve as the others. Oleic, lauric and tridecyllic acids give expanded curves, and would not improbably, if condensed films could be obtained, give the same curve. Cerotic acid behaves much as it did on distilled water, and does not give a proper film. Therefore the only real exception to the rule that fatty acids, saturated and unsaturated, on dilute HCl , give this curve, is iso-oleic acid. This substance had a very similar compression curve (fig. 2, IV), but the slope of the lower portion was less steep, cutting the abscissa at a mean area of $28.7 \text{ \AA.U.}$, the mean of six experiments on two specimens, both prepared by Dr. Le Sueur.

There is no hysteresis in these curves, points obtained by removing weights from the pan and increasing the area lying on the original curve of compression. In this respect they are different from fig. 2, II, which records the behaviour of fatty acids on fresh distilled water, and will be discussed later.

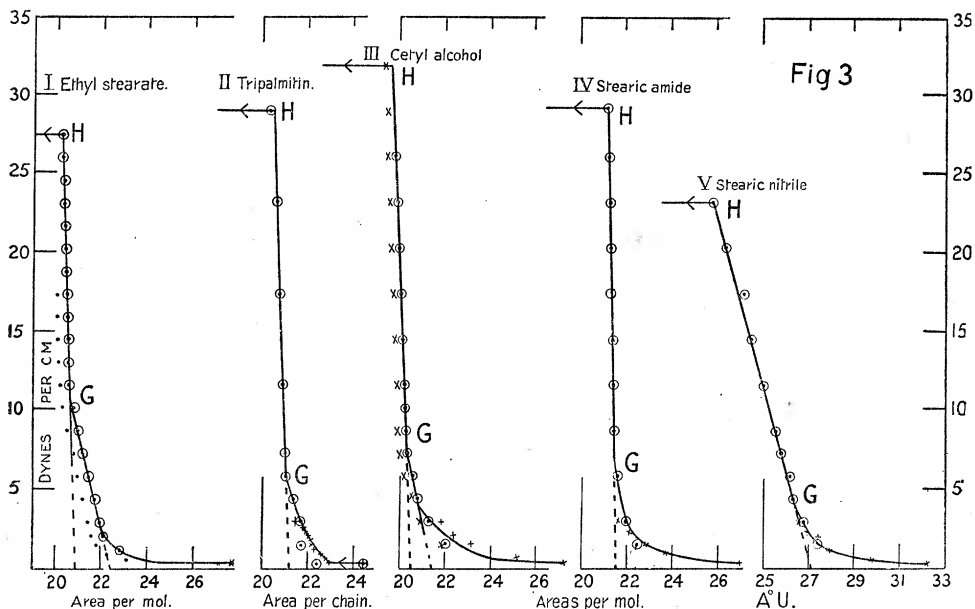
The mean intersection of the lower part with the abscissa is $25.1 \text{ \AA.U.}$

* *Loc. cit.*, p. 346.

5. Esters, Alcohols, Amides, Nitriles and Glycerides.

Fig. 3, I, gives the compression curve of condensed films of ethyl stearate. Ethyl palmitate and ethyl behenate were identical within the experimental error, and methyl palmitate was very similar. The curve may be taken as a typical curve for a condensed film of an ethyl ester. Below the portion GH there is another nearly straight line cutting the abscissa at 22.3 Å.U. mean value.

Cetyl alcohol (fig. 3) has a similar though less easily seen lower portion,



cutting the abscissa at 21.7 Å.U., the mean of eight experiments. This curve is unaltered on HCl.

Tripalmitin (fig. 3, II) shows a slight spontaneous contraction when a low compression is first applied, which is very likely due to the film being very rigid, so that when first put on it is rather in the form of "islands," which do not fit well enough to occupy quite the whole area; and some external compression is necessary to deform these so as to fill the interstitial spaces. Otherwise the curve resembles very closely that of fatty acids on old distilled water. It is doubtful whether there is a distinct lower portion as with cetyl alcohol and the ethyl esters, but, if it exists, its point of intersection with the abscissa is not more than 22 Å.U. The same curve is obtained on HCl. This curve is also given by glycol dipalmitate and tristearin, as would be expected.

Stearic amide (fig. 3, IV) does not show any definite deviation from GH except the tendency to become horizontal, at the lowest compressions, which is common to all the condensed curves, and will be discussed later.

Films of stearic nitrile (fig. 3, V) show an extremely marked lower portion; indeed (though this may yet prove to be attainable), the line GH has not yet been reached in an experiment on this substance before collapse set in. The intersection with the abscissa is at 27.5 Å.U.

Esters of alcohols higher than ethyl have also been tested, but since these films even at the lowest temperatures were expanded, they do not afford evidence as to the cross-section of the molecules. Cetyl palmitate has not yet been tried.

These results are in general agreement with Langmuir's original observations (5). His curve for ethyl palmitate, taken at 16°, is that of a partially or completely expanded film, and this film is only completely condensed below about 6°. He stated, however, that tristearin changed on HCl in the same manner as the acids, which is incorrect. The curves he gave do not agree very well in detail with mine, but his technique was not well suited for avoiding leakage of the film at the barriers.

6. *Cross-section of some Polar Groups.**

The existence of these lower, but quite definite, portions of the curves shows that the films cannot in all cases be regarded as composed of molecules whose *chains* are close packed. For several reasons, there can be little doubt that the molecules are in direct contact all over the area where this type of curve is found. In the first place, the form does not in the least resemble that of the curve of an expanded film (Part III); as with other condensed films, variation of temperature over a considerable range has no effect; and, in every case yet studied, when the temperature is raised sufficiently, the films do pass into the expanded condition in the usual way. It is therefore practically certain that these curves are those of condensed films.

The area is greater than that of the hydrocarbon chains, so that it is clear some part of the molecules have a greater cross-section than the chains. This part must, moreover, be located in the head of the molecule. The area per molecule at which the lower line of a curve cuts the abscissa is the maximum cross-section of the head, as packed in the films. A slight extrapolation is required, but as this portion of the curve is generally nearly straight, it may be made without error. Whether this is really the area of cross-section of the head group which would be occupied in free space is not certain.

* The polar end of the molecule directed towards the water will be called the head, and the hydrocarbon chain, the chain, for brevity.

Table I gives the collected results obtained as to the principal dimensions of various molecules in the films. The lengths of the molecules are not measured directly, but have been deduced from the measurements of area on the possibly dubious assumption that the density in the films is nearly the same as in the acids in bulk. 0.85 has been taken as its value and 21.0 as the area throughout.

$$\text{Length} = \frac{\text{Mol. wt.}}{21.0 \times 6.06 \times 0.85} \times 10^{-7} \text{ cm.}$$

Table I.—Principal Dimensions of Molecules.

Substance.	No. of C's.	Head group.	Cross-sections Å.U. (As packed in films).		Approximate length (Å.U.).
			Chain.	Head.	
Myristic acid	14	—CH ₂ —CH ₂ —COOH	21.0	25.1	21.1
Pentadecylic acid....	15	—CH ₂ —CH ₂ —COOH	21.0	25.1	22.4
Stearic acid	18	—CH ₂ —CH ₂ —COOH	21.0	25.1	26.2
Behenic acid.....	22	—CH ₂ —CH ₂ —COOH	21.0	25.1	31.4
Iso-oleic acid	18	—CH=CH—COOH	21.0	28.7	26.2
Octadecyl urea.....	19	—NH—CO—NH ₂	21.0	26.3	28.8
Stearic amide	18	—CONH ₂	21.0	not greater than 21.5	26.1
Ethyl palmitate ...	18	—COOC ₂ H ₅	21.0	22.3	26.1
Ethyl behenate.....	24	—COOC ₂ H ₅	21.0	22.3	34.0
Cetyl alcohol	16	—CH ₂ OH	21.0	21.7	22.4
Stearic nitrile	18	—CH ₂ CN.	21.0*	27.5	—

* Not measured directly.

It is remarkable that the presence of the double-bond in iso-oleic acid increases the space required by the head to nearly 15 per cent. more than that occupied by the heads of the other fatty acids.

7. The Mechanism of Rearrangement under Compression.

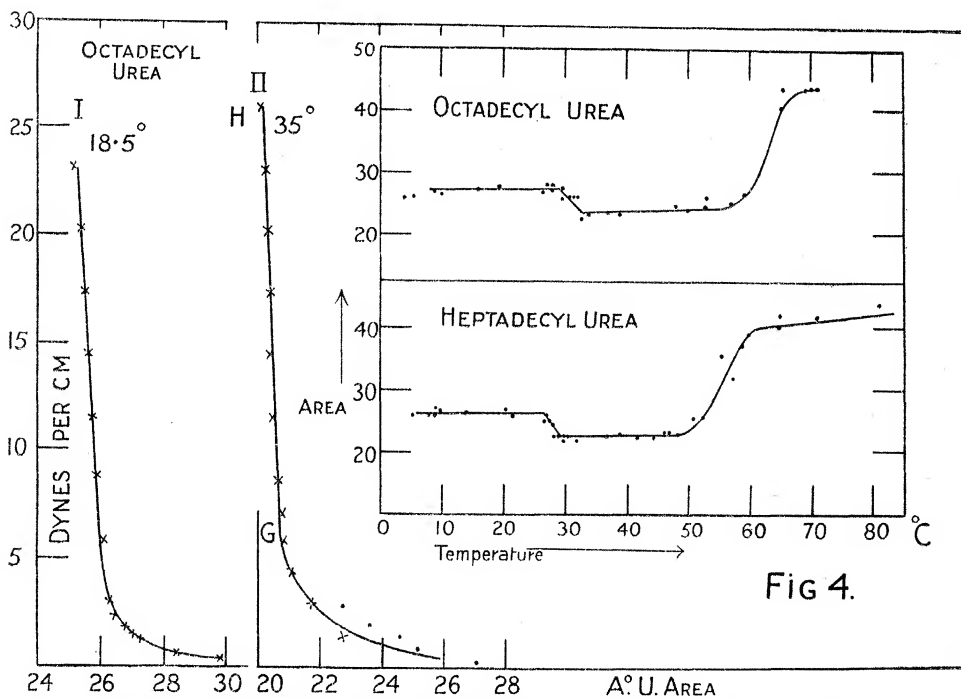
In the majority of cases the curves show that simple compression is all that is required to force the molecules in a film from the state in which they are touching at their heads only into the arrangement with close-packed chains. Either the heads themselves must be compressible laterally, with or without a corresponding elongation in the direction of the chain; or, the heads not being sufficiently easily deformed, they must be moved out of the way by a vertical relative movement of adjacent molecules, the wider portions of some finding recesses in the chains of others, so that the total area becomes no greater than that of the cross-sections of the chains.

There is no evidence to enable a choice to be made definitely between these possibilities. It was suggested in the previous paper that the molecules were displaced, and in the next paragraph it will be shown that the head of the

urea derivatives is, below a certain temperature, practically as incompressible laterally as is any other molecule in bulk, but there is no direct evidence as to the deformability or otherwise of the other groups investigated. It is possible that further evidence on the types of film which show one or the other curve may afford the means of making a decision; and this will lead to some information as to the vertical distribution of molecules in the film, or the depths to which the various molecules are immersed in the water.

8. *The Derivatives of Urea.*

Fig. 4 shows the compression curves obtained on octadecyl urea at two temperatures. They were confirmed on the next lower homologue, heptadecyl urea ($C_{17}H_{35}.NH.CO.NH_2$). Inset are some determinations of area at an



In the inset diagram the areas are at a compression of 1.4 dynes per cm.

arbitrary small compression (1.4 dynes per cm.) plotted against temperature for the two substances. The final rise in these two curves is the ordinary transition to the expanded state common to all substances yet tried; the fall in area between 29° and 33° for octadecyl urea and between 26° and 29.5° for heptadecyl urea is peculiar to these substances, and is a transition from one condensed film whose compression curve is curve I to another, curve II. The compression curve II shows that very little compression is necessary to pack

the chains closely above the temperature of transition. The curve I shows that no amount of compression will pack the chains closely, however, below the transition temperature. Near the transition temperature there is a short region, not yet fully investigated, where the curves are of an intermediate type, but this range of temperature is of a few degrees only. The curve I gives the cross-section of the heads 26.3 Å.U. (mean value). Probably the reason for the heads offering such resistance to compression or displacement is connected with the fact that these substances have more complicated heads than any of the others investigated; and the powerful orienting and cohesive forces between these heads is also indicated by the solidity of the films below the transition temperature; also the study of the expansion of the films of these substances has given an indication that the cohesive forces are greater than between other molecules of the same length of chain. Whatever is the cause, these two substances are the only ones yet found which show two types of condensed film, with a definite transition temperature between them. Further experiments are intended as soon as possible upon other substances possessing yet more complicated heads.

9. *The Physical State of the Condensed Films.*

As was pointed out in the preceding paper, as well as by Langmuir and others, the films are either solid—that is, circulation tangentially of moles on the surface is stopped—or liquid. The fatty acids, amide, glycerides, and esters all can give solid films when the chains are close packed, though occasionally for some unknown reason, in an individual experiment, the film is not always solid. Some of these films are obviously more rigid than others; the glycerides and glycol dipalmitate are the strongest: and the simple fatty acids and esters the least strong of these solid films, and there is some indication that iso-oleic acid gives stronger films than the saturated acids. A long chain seems to give a more rigid film than a short one. On the other hand, cetyl alcohol films are never solid (as Langmuir first pointed out). Therefore close packing of the chains alone is not a sufficient condition for solidity. The only case yet found of a film being solid in which the heads alone are close packed is that of the ureas. Stearic nitrile and the fatty acids on HCl, below the portion GH, are never solid. Probably the factors which determine the solidity or otherwise depend on small details of the shape of the molecule which may be beyond the power of experiments of this type to detect. No observations have yet been made on the temperatures of transition of the solid into the liquid films; in the previous paper a reference was made to the phenomenon of expansion as “melting,” incorrectly, since a more proper term would have been “vaporisation.”

10. *The Effect of Age of the Distilled Water.*

A curious effect exists for which no explanation can be given until more experiments have been done, but it must be noticed briefly as if overlooked it is liable to cause confusion in the experiments. Of the substances yet examined, only the fatty acids show the phenomenon; and the solution must be near to a hydrogen ion concentration of $P_H 6$.^{*} If experiments are done soon after the water (or solution) is put in the trough, the film will temporarily resist a compression of 1.4 dynes per centimetre at an area of about 25 Å.U. There is then fairly rapid contraction to the normal area for close packed chains, completed in about 15 minutes. If weights are put in the pan quickly a curve is obtained like fig. 2, II, the film contracting continually until the line GH is reached. Once this line is reached, further compression merely alters the area along this line; if weights were removed, usually there was little expansion to the right of the line. This, and a perhaps similar phenomenon, which occurs in the transition region of temperature where one type of the urea films is changing into the other, are the only cases yet found in which there is any hysteresis in the monomolecular films.

If, however, the water or solution is allowed to remain in the brass trough for about 5 days before an experiment, fig. 2, I, is obtained, showing that the chains pack themselves closely almost immediately. What is the change which takes place in the water to alter the films in this manner has not been discovered. It is not the solution of small amounts of fatty acids in the water, for it makes little difference whether experiments have been done on the water during the 5 days "seasoning" or whether the trough has been undisturbed with a cover over it. It is not a change in the hydrogen ion concentration, as it has been noticed on solutions containing phosphate buffers in which the P_H remained constant within 0.1. CO_2 free water, and water nearly saturated with CO_2 at atmospheric pressure, behave like fresh water at first. It makes no difference whether the water has been condensed in silver, tin, or copper, during distillation. Glass distilled water has not yet been investigated for this effect. That the action is on the carboxyl groups is rendered probable by the fact that only the acids show the change.

[*Note added, June 18.*—Water condensed and preserved in glass and used in a glass trough, without any contact with metal, behaved in the same way as the waters mentioned above.]

* A P_H of 6 denotes a hydrogen ion concentration of 10^{-6} normal.

11. *Solubility of the Films.*

A good deal of qualitative information has been accumulated on the rate of solution of the various substances in the water. The number of molecules passing into solution may be determined without difficulty by observations of any steady decrease in area which occurs under conditions where leaks or measurable spontaneous accumulation of contamination or collapse are absent; and there is usually no difficulty in allowing for small amounts of contamination, if present, by a blank experiment. Solution cannot of course be distinguished from volatilisation directly, but since the rate of disappearance of the substances studied always increased with conditions favouring a stronger attraction between the film and the water, it is improbable that volatilisation was the cause of the contraction.

Solubility depends on a balance in the molecule between the number of polar groups having a strong attraction for the water, and the length of the hydrocarbon chains. The former increase, the latter decrease solution. Higher temperatures accelerate solution.

Upon dilute (N/100) HCl, the rate of solution of all the fatty acids down to lauric is inappreciable at room temperature. On nearly neutral solutions solubility of the acids up to pentadecylic may be noticeable. Addition of one carbon atom to the chain very much decreases solubility. When the C_{15} acid is insoluble, and the C_{14} film decreases at about 1 per cent. per minute, a film of tridecylic acid will disappear about ten times as fast, and the C_{12} acid so fast that before any measurement of area can be taken probably about one-third of the film will have disappeared. Near neutrality, the seasoning effect just mentioned decreases solubility; allowing the solution to stand undisturbed 3 days rendered the solubility of the C_{14} acid inappreciable, while on a fresh solution of the same composition, the C_{15} acid film dissolved at a measurable rate. It was rather surprising to find that for acids above C_{16} , it was possible to obtain approximate measurements of area on N/10 soda, solution taking place only slowly.

12. *Spontaneous Expansion of the Films.*

In two instances the films expanded slowly in area. These were octadecylamine hydrochloride, on distilled water, and cetyl alcohol on a phosphate solution. Cetyl alcohol films did not expand on distilled water. The rate of expansion, at room temperature, was initially about 8 per cent. per minute for the amine hydrochloride, and 0.2 per cent. per minute for the alcohol. The former rate fell off rapidly with the time, and the latter was not much changed after $\frac{1}{2}$ an hour.

Such phenomena must be due to a slow combination of the end group of

the film molecule with some constituent of the underlying solution, resulting in an increase of cross-section; and it is possible that measurements of the rate of expansion may give useful information concerning the progress of some chemical reactions, when the structure of the films is better understood. It is an interesting confirmation of the view that in the condensed films the molecules are closely packed, while in the expanded they are not, that this expansion of the amine hydrochloride film continues up to the temperature at which the expansion becomes nearly complete, but ceases at higher temperatures. The increase in cross-section of the heads of individual molecules may occur, but it is not shown in an increase of the area of the film, unless the molecules are in contact.

13. *Collapse of the Films under Higher Compressions.*

No important difference from the behaviour of palmitic acid films previously described (Part I, p. 348) has been found with any of the substances here investigated. The force required to start collapse is variable. The observation of Labrouste, that when the aggregates ejected from a film are solid they do not spread again into a monomolecular film on removing the compression, has been confirmed. This does occur if the aggregates are liquid.

14. *Form of the Curves at very Low Compressions.*

It was left doubtful in Part I whether or not there was a real deviation from the general linear direction of the curves at the lowest compressions. The lowest forces there measured were 1.4 dynes per centimetre. Later measurements made down to one-fifth of this amount, and, shown in the diagrams, have proved fairly consistent, and show, in all cases, a tendency of the curves to become horizontal at no compression.

If the theory that the expansion of the films, to be described in Part III, is due to the escape of molecules from the condensed or close-packed films is correct, some kind of "vapour pressure" should be expected in the surface, with condensed films below the temperature of expansion. It is possible that this is the cause of the approach to the horizontal in the region now considered. In none of the curves does there appear, however, a horizontal or nearly horizontal, line of any length at a distance from the abscissa greater than 0.4 dynes per centimetre, until the temperature has risen into the transition region between condensed and expanded films (see the next paper), that is, within some 20° of the temperature at which the films are practically completely expanded. The force of 0.4 dyne per centimetre is, on a film of thickness equal to the length of molecules of stearic acid, about 1.5 atmospheres pressure. Thus the pressure exerted by molecules escaping from the

condensed parts of the film increases very sharply as the temperature approaches that of complete expansion.

A fairly sharp intersection of a horizontal line representing the vapour pressure, with the direction of the curve of the condensed film, would be expected on this hypothesis; actually, however, there is no sharp angle but an easily curved line. Possibly the rounding off is due to residual contamination, though in some cases the effect seems rather large to be accounted for in this way; or, there may be some other form of condensed film in which the molecules are in contact in some arrangement very easily disturbed by slight external compression—the arrangement requiring, perhaps, greater cross-sections than those given in Table I. The experiments are not, however, accurate enough to provide real evidence of the existence of any new condensed state.

15. *Experimental Details.*

To the description of the method of experiment given in the preceding paper, some details should now be added. The simplest way of drying the trough after cleaning is to rinse it with boiling water; then it is immediately placed on the levelling screws, the top of the sides wiped dry, if necessary, with clean filter paper, and a solution of paraffin wax in benzene put on with a glass rod, while the trough is warm. The barriers and float are paraffined with the same solution and dried in an oven before use. The use of paraffin wax is absolutely essential to prevent leakage past the barriers, and the top of the sides of the trough must be accurately flat, in order that the glass barriers may touch over the whole width.

Leakage past the floating barrier has been watched for, and the position of the air jets at A and B (fig. 1) adjusted till all leak was stopped. Leaks are one of the most frequent sources of error, and constant vigilance is necessary. Rack and pinion and screw adjustments, giving up and down, side to side, and forward and backward motion, have very much diminished number of failures and the labour of attending to an experiment. It is necessary also to adjust the strength and direction of the air blast so that the balance maintains a constant zero. This can be done with a little experience, without diminishing the strength so much as to allow leaks to occur under high compression.

No correction has been applied for residual contamination. Its total amount has been always small, and it is thought that none of the areas here recorded at temperatures below 35° C. are so much as 2 per cent. too great, from this source of error, where the compression has been greater than about 3 dynes per centimetre. At the lowest compressions measured, this error probably does not exceed 8 per cent. From 35° to 55° C. contamination has

been slightly more troublesome, but probably doubling these limits is sufficient. Above 55° , when the paraffin coating on the sides is melted, it is very difficult to obtain more than three reliable points before the contamination becomes serious; however, by working rapidly, these points may be determined with little more error than below 55° .

Points over the whole range of compressions have generally not been determined in a single experiment. Such a procedure would tend to give too high areas in the later part of the experiment, because a good deal of time must be spent in determining the areas below 3 dynes per centimetre, and at the low compressions the rate of contamination is appreciable. The usual plan has been to determine about five points between 0.35 and 2.8 dynes in one experiment, and in another to commence at 1.4 dynes and add successive increments of 1.4 dynes or 2.8 until the film collapses.

A useful check on the value of a single experiment is afforded by removing weights from the pan. If there has been any leakage or solution of the film there is apparent hysteresis, and an idea can be obtained of the amount of error by comparing the curves of contraction with those of expansion. Any accumulation of contamination acts in the opposite direction to the last two sources of error. Except for the two cases of rather special character mentioned in Section 10, p. 466, I have not yet found a case of real hysteresis among monomolecular films.

The temperature of the trough was regulated by two or three small burners below. There was no difficulty in keeping it constant and uniform to 1° below 35° , to 2° up to 60° , and to 3° up to about 70° . The temperature was read by a thermometer placed in the trough, and it was verified that this indicated the temperature of the surface, by determining the melting point of floating particles of palmitic acid.

Where the substances were not sufficiently soluble in benzene, a small amount of alcohol was added.

The bar F in the diagram was employed for steadying the dropping pipette E, used for measuring the quantity of substance put on. With care, the error in knowing the amount put on should not exceed 3 per cent. in one experiment. The number of molecules in a gramme molecule has been taken as 6.06×10^{23} .

16. *Preparation and Purification of Materials.*

The saturated fatty acids employed all melted within half a degree of the accepted melting point of the pure substances. Titration in alcoholic solution showed the molecular weights of all those with an even number of carbon atoms to be correct within 1 part in 200, except stearic acid, which as finally

purified had a molecular weight about 0.8 per cent. too low. The acids of an odd number of carbon atoms and the $\Delta\alpha\beta$ -oleic acid were prepared by Dr. Le Sueur, and were undoubtedly of the highest purity when prepared. Verification of the melting points disclosed no sign of deterioration. Oleic acid was an exceptionally pure specimen, prepared in Prof. Lapworth's laboratory. Elaidic, erucic, and brassidic acids had the correct molecular weights. The iodine values were correct for elaidic acid, and indicated about 5 per cent. of admixed saturated acids, probably behenic, for the erucic and brassidic acids. The melting points were those given by Lewkowitsch (6) except brassidic (61° – 62° instead of 65°).

Cetyl alcohol was purified till it melted at 50° . Stearic amide and nitrile were prepared from pure stearic acid and purified till they melted constantly at 109° and 42° respectively.

Octadecylamine hydrochloride was prepared by reducing stearic nitrile with sodium and alcohol (7). It was precipitated twice from alcohol by ether; m.p. indefinite, but above 160° . Octadecyl urea was prepared from the preceding by treatment with the theoretical quantity of potassium cyanate; m.p., constant, 111° . Nitrogen, found by the Kjeldahl method, 8.85 per cent.; theoretical, 8.98 per cent.

Heptadecylamine was obtained from stearic amide by the modification of the Hoffmann reaction described by Jeffreys (8); m.p. 54° – 56° after redistillation from sodium and boiling to remove CO_2 and water. Heptadecyl urea from the preceding melted constant at 108 – 9° , agreeing with Jeffreys' determination.

The esters of palmitic acid were prepared by warming together the purified alcohol and palmityl chloride and recrystallising the product from dilute alcohol. M.p.'s: methyl palmitate 29.5° – 30° , ethyl 25.5° , *n*-propyl 15° – 16° , *n*-butyl 13° – 14° , iso-butyl 19° – 23° , iso-amyl 11° – 12° , *n*-octyl 24° – 25° . Other esters were prepared in the usual way. A few specimens were found by titration to contain small amounts of free acid (as palmitic), up to 2 per cent.

Tripalmitin and tristearin were purified to have the correct saponification values within 0.6 per cent.; m.p.'s: 63 – 4° and 68.5° – 69.5° .

Glycol dipalmitate had the m.p. 70° ; this appears to have been incorrectly recorded in the original paper as 65° by a clerical error (9). The specimen was the original one prepared by Miss Stephenson.

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The Corrosion of Iron and Steel.

By Sir ROBERT HADFIELD, Bt., F.R.S.

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Introduction.

The subject of the corrosion of iron and steel is a most important one, yet with the exception of a minor contribution by Dr. E. Newbery and the author in 1916, no communication has been presented to the Royal Society for the last one hundred years. This paper refers to the wastage of the world's iron and steel due to corrosion, and describes a number of recent experiments carried out by the author with regard to copper-steel. It is hoped that these results will add to the general knowledge on this subject of corrosion from both the scientific and practical point of view.

Careful estimates appear to show that there is a present annual loss of over 40 million tons of iron and steel under corrosion and consequent removal of material rendered unserviceable. Taking into account the cost of protecting the material, the author estimates that the aggregate annual loss due to the effects of corrosion is probably well over 500 million pounds sterling, based on prices which have prevailed during the last few years.

The introduction of alloy steels which possess high capacity for resisting corrosion should be encouraged, and although higher in the first cost they will probably be found more economical in the long run.

The great importance of economy in the use of iron, and of studying methods to avoid or reduce rusting or oxidation, is shown by valuable and interesting statements in a recent article, 'Iron Ore in Europe,' by Prof. J. W. Gregory, one of our Fellows. In reviewing a report by Mr. Max Roesler, of the U.S.